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FIREPROOF WATER GLASS COMPOSITE BASED ON MECHANICALLY ACTIVATED ALUMINA

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The effect of the silica modulus of water glass, functional additives, and mechanical activation of the filler on the composition of a fireproof composite is described. At temperatures up to 700°C one can decrease thermal diffusivity by the formation of a heat-insulating layer frothed by water vapor dehydrated from water glass. Within the high-temperature range heat-insulating properties are improved by the synthesis of nepheline in the reaction between sodium silicate and alumina. Mechanical activation of alumina improves this effect. Introduction of carbamide and boric acid additives improves the fireproof properties of the gaseous medium.

Comprehensive antifire prophylactics should be supported by a new generation of environmentally safe and cost-effective fireproof composites with good service parameters. Water glass, which for 50 years has been used as a binder in such composites, meets the requirements on environmental safety, availability, and low-cost technology. At the same time the existing level of properties of fireproof composites based on water glass does not satisfy consumer needs with respect to their durability, working life, and fireproof efficiency for coatings with a low covering power [1] and calls for substantial improvement.

The purpose of our study was to select an optimum qualitative and quantitative composition for fireproof composites based on water glass ensuring a high level of properties.

The studies were performed on mixtures with sodium water glass as the most extensively used product (GOST 13078). The filler was alumina G-00 (GOST 30559). The chemical inertness of alumina to water glass had to ensure a long working life of the composite and the durability of the coating. The structural state of alumina was modified by mechanical activation in air in a planetary-centrifugal mill in rubberized drums with corundum balls; the material : balls ratio was equal to 1 : 3 and the drum acceleration was equal to 18g. According to adhesion measuring data, the optimum duration of mechanical activation is 30 min. An increased formation of particle aggregates under a longer activation results in poorer adhesion. The fireproof effect for metal was determined according to GOST 30247.0 and for wood according to GOST 16363. The low-temperature state of composites was analyzed by IR spectroscopy with a Spekdord 75 IR instrument and its state after a high-temperature effect was analyzed with a DRON-3M diffractometer.

The fireproof effect of the composite is due to the formation of a heat-insulating layer, a protective atmosphere, and to endothermic processes that lower the surface temperature [2]. We have established that the frothed layer thickness and the thermal diffusivity of water glass significantly depend on silica modulus n and are proportionate to weight losses (Fig. 1). Weight losses are caused by the removal of chemically fixed water after crystallization within a temperature range of 100–600°C. With a decreasing silica modulus the content of this water increases [3]. The most effective heat-insulating layer is formed using water glass with $n = 2.2–2.5$. With $n < 2$ the increased water-retaining capacity of the medium virtually stops crystallization and drying of the film.

The increase in thermal diffusivity in the high-temperature range is notable (Fig. 2). This can be explained by the decreasing thickness of the plastic frothed layer of water glass crumpled by the hot gas flow from the gas burner and by the sintering processes. The increased porosity of com-

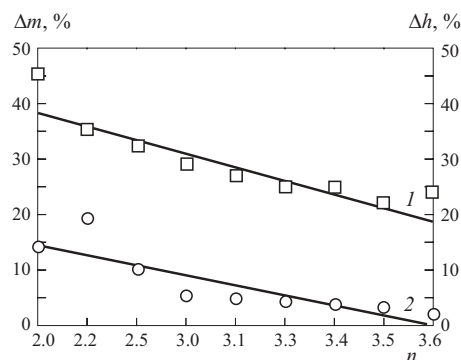


Fig. 1. Weight loss Δm (1) and layer thickness variation Δh (2) in water glass depending on silica modulus n .

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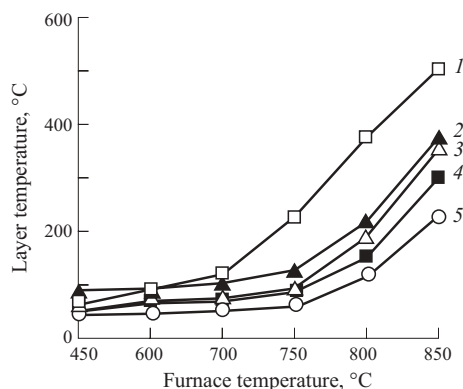


Fig. 2. Thermal diffusivity of water glass layer with $n = 3.6$ (1), 3.1 (2), 3.0 (3), 2.2 (4), and fireproof composites with water glass ($n = 2.2$) and mechanically activated alumina (5).

posites containing water glass with a low silica modulus retards sintering and the growth of thermal diffusivity. The introduction of mechanically activated alumina has a positive effect on lowering the thermal diffusivity in the high-temperature range. According to x-ray phase analysis data, mechanically activated alumina reacts more intensely with water glass and forms a nepheline phase which during the initial stages is localized along the grain boundaries and creates sintering stoppers [4]. Furthermore, the new and the original phases differ significantly in their elementary cell volume V , which should facilitate the emergence of diffusion porosity (Table 1).

The efficiency of creating a protective atmosphere was studied on a group of thermosensitive compounds with a fireproof effect: H_3BO_3 , $(\text{NH}_2)_2\text{CO}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

It is found that the entire process of wood destruction from the start of combustion (the first 2 min of thermal treatment) and subsequent evolution (after 4 min) is not covered by the temperature interval of decomposition of any of the above compounds. At the same time, the start of combustion most closely coincides with the decomposition of carbamide, whereas the stage of combustion evolution coincides with the decomposition of boric acid (Fig. 3). The optimum com-

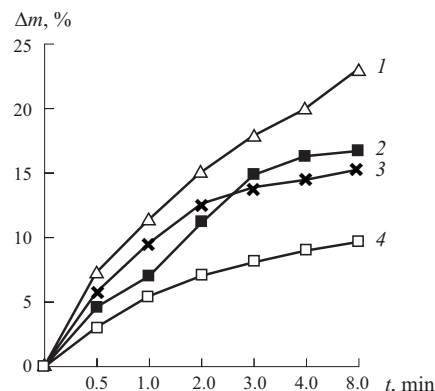


Fig. 3. Weight loss Δm of pure wood (1), wood with carbamide (2), with boric acid (3), with carbamide and boric acid (4).

bination of these additives is equal to 3.5 and 3.0 wt.%, respectively [5]. Such composite has an increased fireproof efficiency. The weight loss of wood after depositing this coating does not exceed 5–6%.

The presence of carbamide in composites based on water glass has a positive effect on their properties [6]. This effect is intensified when using mechanically activated alumina. A sharp increase in the adhesion, working life, and durability of coatings has been established (Table 2). Presumably the mechanical activation of the filler expands the function of carbamide, which not only participates in the polymerization of silazan links in water glass molecules [6] but also forms chemisorption bonds with the activated filler surface.

The IR spectra of the composite with mechanical activated alumina exhibit the extinction of the absorption band corresponding to the symmetric valence vibrations of the amide group in carbamide νNH_2 (Fig. 4) [7]. A similar phenomenon was observed in increasing the number of nitrogen atoms from 3 in NH_3 molecule to 4 in $(\text{NH}_4)^+$ cation [8]. An additional bond may be formed between the N^{3-} amide groups and the surface of $\gamma\text{-Al}_2\text{O}_3$ particles contained in alumina. The x-ray pattern of this phase does not have the reflection $d = 0.456$ nm. The formation of chemisorption bonds does not result in coagulation, unlike the chemical reactions between water glass molecules and fillers based on

TABLE 1

Phase	Syngony	Cell parameters, nm		V , nm ³	Parameters of alumina G-00 reflection		
		a	c		d , nm	I_{rel} , %*	
						initial	mechanically activated
α -Al ₂ O ₃	Hexagonal	0.476	0.130	0.026	0.26	100	100
γ -Al ₂ O ₃	Cubic	0.790	—	0.493	0.14	47	37
NaAlSiO ₄	Hexagonal	0.998	0.833	0.718	0.43	20	93

* Treatment temperature 800°C.

TABLE 2

Parameter	Alumina G-00		Control method
	initial	mechanically activated	
Adhesion at temperature of $20 \pm 0.5^\circ\text{C}$, MPa, at least	0.7	3.0	GOST 15140
Fireproof properties:			
duration of independent combustion, sec	0	0	GOST 30244
combustibility group for wood	1B	1B	GOST 16363
group 5 of fireproof efficiency			
with thickness of coating on metal, mm	1.0	0.6	GOST 30247.0
group 4 of fireproof efficiency			
with thickness of coating on metal, mm	3.0	2.2	GOST 30247.0
Warranty, years:			
service life of coating (durability)	3	8	—
storage in airtight package since manufacture date (working life)	1	2	—

Thus, the thermal diffusivity of a fireproof composite in the low-temperature range depends on the quantity of dehydrated water determined by the silica modulus. In the high-temperature range the synthesized nepheline phase has an additional effect on modifying thermal diffusivity. Mechanical activation of alumina accelerates synthesis and lowers thermal diffusivity. A combined additive of carbamide and boric acid improves the fireproof properties of the gaseous medium. Carbamide impedes inflammation and the acid impedes the evolution of the combustion process. The introduction of mechanically activated alumina improves a number of technical properties of the composite.

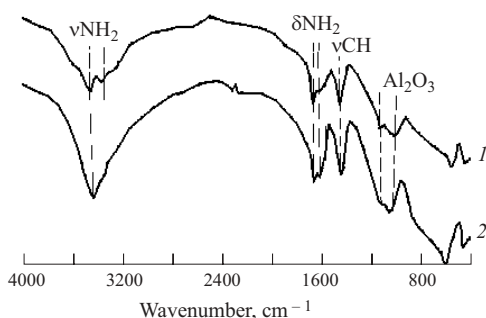


Fig. 4. IR spectra of composites with initial alumina (1) and alumina mechanically activated in air for 30 min (2).

Mg^{2+} and Ca^{2+} [3]. The properties of the fireproof composite based on alumina are listed in Table 2.

The fireproof composite with mechanically activated alumina has been certified by the state and its experimental production has been started at the Korund Ltd Company.

REFERENCES

1. I. G. Romanenkov and F. A. Levites, *Fire Protection of Constructions* [in Russian], Stroiizdat, Moscow (1991).
2. L. N. Mashlyakovskii, et al., *Organic Coatings with Decreased Combustibility* [in Russian], Khimiya, Moscow (1989).
3. V. I. Korneev and V. V. Danilov, *Soluble and Water Glass* [in Russian], Stroiizdat, St. Petersburg (1996).
4. Ya. E. Geguzin, *Physics of Sintering* [in Russian], Nauka, Moscow (1984).
5. N. V. Eremina, V. Yu. Zelinskii, and E. G. Avvakumov, "Fireproof composite based on water glass and mechanically activated aluminum oxide," *Khim. v Interesakh Ustoichivogo Razvitiya*, **12**(3), 331 – 337 (2004).
6. P. B. Razgovorov, V. A. Ignatov, Z. Ts. Koifman, and I. N. Terskaya, *Izv. Vuzov, Ser. Khim. Khim. Tekhnol.*, **36**, Issue 1, 68 – 70 (1993).
7. J. Gradolnik and Y. Marechal, "Urea and urea-water solutions — an infrared study," *Molecular Struct.*, **615**, 177 – 189 (2002).
8. A. I. Boldyrev, *Infrared Spectra of Minerals* [in Russian], Nedra, Moscow (1976).